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(54) Title: SCREEN PRINTABLE ADHESIVE COMPOSITIONS (57) Abstract A screen printable adhesive composition comprising 25 to 100 parts by weight of at least one alkyl acrylate monomer and 0 to 75 parts by weight of at least one reinforcing comonomer, wherein said composition is substantially solvent free and has a yield point of less than 600 dynes/square centimeter and a viscosity of less than 4000 centipoise.		

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SCREEN PRINTABLE ADHESIVE COMPOSITIONS

5 Field of the Invention

The present invention relates to screen printable adhesives.

Background of the Invention

Screen printing of adhesives is known in the art and is used advantageously
10 to apply adhesives to selected areas on a substrate. The adhesive printed or coated
areas can subsequently be used to adhere to a second substrate. Typical screen
printable adhesives are pressure-sensitive adhesives which are tacky at room
temperature, or heat activatable adhesives, which are not tacky at room
temperature, but become tacky when heated. Examples of screen printable
15 adhesives include a (meth)acrylic polymers and co-polymers dispersed in an organic
solvent or water.

Acrylic adhesives, both pressure-sensitive and heat activatable types, are
widely used in industry because they are stable over time, and they can be
formulated to adhere to a wide variety of different surfaces. Typical acrylic
20 adhesives are prepared as taught in U.S. Patent No. RE 24,906 (Ulrich). With the
advent of more stringent environmental controls, the technology in adhesives in
general has evolved from solvent based materials to water-based materials, and to a
degree, solvent-free materials. Solvent-free acrylate adhesives are known and fall in
various categories of processing such as heat activatable coating and radiation
25 curing which includes E-beam curing, ultraviolet light processing, and gamma
radiation processing. Solvent-free thermosetting compositions are known in the art,
but they would provide little utility for adhesively bonding to other substrates since
they are highly cross-linked and do not flow or become tacky on heating.

Solvent free screen printable adhesives are also available commercially that
30 are cured by radiation induced cross-linking. Generally, these adhesives do not
have good shear strength.

Ultraviolet light processed adhesives are described in U. S. Patent No. 4,181,752 (Martens et al.). While known adhesives processed by ultraviolet light have their own utility and advantages, they do not screen print well because they tend to become stringy during screen printing. Therefore, an ongoing need exists
5 for pressure-sensitive and heat activatable adhesives that are solvent-free, can be screen printed without the use of solvent, and provide good shear strength and peel strength.

Summary of the Invention

10 The invention provides a screen printable adhesive composition comprising:

(a) 25 to 100 parts by weight of at least one alkyl acrylate monomer;

and

(b) 0 to 75 parts by weight of at least one reinforcing comonomer;

wherein said composition is substantially solvent free and has a yield point
15 of less than 600 dynes/square centimeter and a viscosity of less than 4000 centipoise.

In another embodiment, the invention provides a screen printable adhesive composition comprising an acrylate polymer and one or more monomers, said acrylate polymer and one or more monomers comprising :

20 (a) 25 to 100 parts by weight of at least one alkyl acrylate;

(b) 0 to 75 parts by weight of at least one reinforcing comonomer;

(c) an effective amount of at least one chain transfer agent; and

(d) an effective amount of an electrically conductive agent;

wherein said composition is substantially solvent free and said polymer has a
25 weight average molecular weight of from 50,000 to 1,000,000.

Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the methods and articles particularly
30 pointed out in the written description and claims hereof.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

5 Detailed Description of the Invention

The screen printable pressure bondable adhesives of the invention are substantially solvent free acrylic polymers that can be screen printed without requiring the use of additional solvent. As used herein, "pressure bondable" refers to adhesives that are applied to one surface, and will bond to a second surface under
10 pressure. The adhesives include pressure-sensitive adhesives which are tacky at room temperature, and heat activatable adhesives which are substantially non-tacky at room temperature, but will bond at an elevated temperature which is typically in the range of from about 25°C to 200°C.

As used herein, "substantially solvent free" refers to an adhesive that has
15 been prepared without the use of large amounts of solvent, that is, less than 5% by weight of a coating composition, preferably less than about 2%, and more preferably no additional solvent is added. The preparation of the adhesive includes processes used in the polymerization of the monomers present in the adhesive as well as processes used in coating the adhesive to make finished articles, for
20 example, pressure-sensitive adhesive tapes. The term "solvent" refers to conventional organic solvents used in the industry which include, for example, toluene, heptane, ethyl acetate, methyl ethyl ketone, acetone, and mixtures thereof.

The adhesives of the invention are prepared from adhesive compositions comprising from about 25 to 100 parts by weight of at least one alkyl acrylate
25 monomer, and correspondingly, from about 75 to 0 parts by weight of a reinforcing co-monomer.

Monomers useful in the practice of the invention are those which have a homopolymer glass transition temperature less than about 0°C. Useful alkyl
acrylates are unsaturated monofunctional (meth)acrylic acid esters of non-tertiary
30 alkyl alcohols having from 2 to 20 carbon atoms in the alkyl moiety, and preferably from 4 to 18 carbon atoms. Examples of useful alkyl acrylate monomers include,

but are not limited to, n-butyl acrylate, hexyl acrylate, octyl acrylate, isooctyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, decyl acrylate, lauryl acrylate, octadecyl acrylate, and mixtures thereof.

A monoethylenically unsaturated reinforcing co-monomer having a
5 homopolymer glass transition temperature greater than about 25°C is preferably co-polymerized with the acrylate monomers. Examples of useful co-polymerizable monomers include, but are not limited to, meth(acrylic) acid, N-vinyl pyrrolidone, N-vinyl caprolactam, substituted (meth)acrylamides, such as N,N,-dimethyl acrylamides, acrylonitrile, isobornyl acrylate, N-vinyl formamide, and mixtures
10 thereof. When a co-polymerizable monomer is used, the alkyl acrylate is present in the composition in amounts from about 25 to 99 parts by weight and the co-polymerizable monomer is present in corresponding amounts from 75 to 1 parts by weight wherein the total amount by weight is 100.

The amounts and types of co-monomer can be varied to provide pressure-
15 sensitive or heat activatable properties as desired for the end use. Larger amounts of co-monomer will result in less tack and are suitable as heat activatable adhesives while lower amounts are more suitable for pressure-sensitive adhesives. The type of co-monomer can also be varied to obtain desired properties. Polar co-monomers, that is, those which have hydrogen bonding moieties, such as acrylic
20 acid are useful in amounts from about 1 to about 15 parts by weight for pressure-sensitive adhesives. Amounts above about 15 parts are useful as heat activatable adhesives. Less polar co-monomers such as N-vinyl caprolactam, N-vinyl pyrrolidone, and isobornyl acrylate provide pressure-sensitive properties to an adhesive up to about 40 parts by weight, while amounts above about 40 parts will
25 provide heat activatable adhesives.

The screen printable adhesive compositions of the invention are prepared so that they have a yield point and viscosity suitable for screen printing. The yield point is the stress needed to cause the adhesive to flow. Since the compositions would be screen printed on relatively large surface areas, they should flow
30 sufficiently to provide a fairly smooth surface in a short amount of time, that is, within minutes after screen printing. Compositions are selected to provide a yield

point that is low enough to allow the composition to flow after printing. The compositions of the invention preferably have a measured yield point of less than about 600 dynes/square centimeter as determined on a Carri-Med CS Rheometer. If the adhesive composition is filled with particles, the yield point is typically greater than about 100 dynes/square centimeter to help keep the particles in suspension.

The viscosity (Carri-Med CS Rheometer) of the compositions should be low enough for screen printing, but high enough to prevent excessive flow and maintain definition. Preferably, the viscosity of the adhesives is less than about 4000 centipoise (cps), and more preferably, less than about 2000 centipoise, and most preferably less than about 1500 centipoise. Typically, the viscosity is greater than 50, but there is not a specific lower limit if the composition thickens or coalesces upon removal of the screen. Compositions containing particles preferably have a viscosity greater than about 100 cps.

Some adhesive compositions, especially pressure sensitive adhesive compositions, are prone to stringing which makes them undesirable for screen printing. Stringing can be reduced or eliminated by controlling the molecular weights of the polymers and prepolymers in the compositions.

Fillers useful for the invention include fumed silica which will thicken a monomer mixture of the monomers described above or a syrup of the monomers. The silica imparts thixotropy to the mixture which will allow it to thicken after the stress of screen printing is removed.

Stringing can be controlled by adding a thermoplastic polymer or copolymer of appropriate molecular weight, or macromer to the monomer mixture or syrup of the above described acrylates. Preferably, the polymer, copolymer, or macromer has a weight average molecular weight of less than about 100,000. Useful thermoplastic polymers include acrylic polymers such as poly(iso-butylmethacrylate) such as Elvacite 2045 (ICI Americas). Useful copolymers include block copolymers such as styrene butadiene co-polymers and acrylic co-polymers. Useful macromers are those which are co-polymerizable with the acrylate monomers and are described in U.S. Patent No. 4,554,324 (Husman et al.), and are commercially available from ICI Americas (ELVACITE™ 1010). In the practice of the invention,

the polymer, copolymer, or macromer is dissolved in the monomers or syrup. This can be done on conventional equipment such as roller mill, ball mill, and the like. The monomers or syrups can be heated, for example, to about 80°C to enhance dissolution of the polymers or macromers.

5 Stringing can also be reduced in a partially polymerized syrup by adding a chain transfer agent to the monomers before polymerizing to control the molecular weight.

 The chain transfer agents useful in the practice of the invention include, but are not limited to, carbon tetrabromide, n-dodecyl mercaptan, isooctyl
10 thiolglycolate, and mixtures thereof. The chain transfer agent(s) are present in amounts from about 0.01 to about 1 part by weight per 100 parts of acrylate (pph), that is, 100 parts of the alkyl acrylate and the reinforcing co-monomer, and preferably in amounts from about 0.02 to 0.5 pph.

 The weight average molecular weight of the polymers of the useful adhesive
15 compositions, that is, syrup, is between about 50,000 and 1,000,000. Preferably the molecular weight is between about 100,000 and about 800,000, and most preferably, between about 150,000 about 600,000. The lower molecular weights limit the elongational viscosity and result in less stringing of the adhesive during screen printing.

20 In a preferred embodiment, the adhesive composition also includes a thixotropic agent such as silica to impart thixotropy to the composition. The viscosity of a thixotropic composition decreases when it is subjected to shear stresses so that it flows when it is screen printed. Once the shear stress is removed, the thixotropic material increases rapidly in viscosity so that the printed adhesive
25 essentially does not flow once it has been printed onto a substrate. A suitable silica is commercially available silica under the Cab-O-Sil™ trade name (such as M-5 and TS-720) from Cabot Corp. and Aerosil™ 972 Silica from DeGussa.

 In another preferred embodiment, the adhesive composition also includes electrically conductive materials. Such materials include, but are not limited to,
30 metal particles and spheres such as nickel, gold, copper, or silver particles and spheres and particles coated with conductive coatings such as gold, silver, copper,

or nickel coatings on copper spheres, nickel spheres, polymeric spheres or particles, and glass microspheres. Also useful are solder particles such as lead/tin alloys in varying amounts of each metal (available from Sherritt Gordon, Ltd.). Examples of commercially available electrically conductive particles include conductive nickel spheres from Novamet. Inc. Electrically conductive materials are also available from Japan Chemicals, Inc., Potters Industries, and Sherritt Gordon Limited.

Electrically conductive particles can be used in amounts from about 1% to 10% by volume, and preferably in amounts from about 1% to about 5%, by volume.

The compositions of the invention also preferably include free radical initiators. The initiators are known in the art and are preferably light activated. In a preferred embodiment, the initiator is a photoinitiator and examples include, but are not limited to, substituted acetophenones, such as 2,2-dimethoxy-2-phenylacetophenone, benzoin ethers such as benzoin methyl ether, substituted benzoin ethers such as anisoin methyl ether, substituted alpha-ketols such as 2-methyl-2-hydroxypropiophenone, phosphine oxides, and polymeric photoinitiators. Photoinitiators are commercially available from sources such as Ciba Geigy under the Irgacure™ trade designation, such as Irgacure™ 184, Irgacure™ 651, Irgacure™ 369, Irgacure™ 907, under the Escacure™ trade name from Sartomer, and under the Lucirin TPO trade name from BASF.

The photoinitiators can be used in amounts from about 0.001 pph to about 5 pph depending upon the type and molecular weight of the photoinitiator. Generally, lower molecular weight materials are used in amounts of about 0.001 pph to about 2 pph, while higher molecular weight polymeric photoinitiators are used in amounts from about 0.1 pph to about 5 pph.

After the syrup has been formed, cross-linking agents can be added to the adhesive to improve the cohesive strength of the adhesive. Useful cross-linking agents include multifunctional acrylates, such those disclosed in U.S. Patent No. 4,379,201 (Heilman), which include but are not limited to 1,6-hexanediol diacrylate, trimethylolpropane triacrylate, 1,2-ethylene glycol diacrylate, pentaerythritol tetracrylate, and mixtures thereof, co-polymerizable aromatic ketone co-monomers such as those disclosed in U.S. Patent No. 4,737,559 (Kellen), photoactive triazines

such as those disclosed in U. S. Patent Nos. 4 329,384 (Vesley, et al), 4,330,590 (Vesley), and 4,391,687 (Vesley), organosilanes, benzophenones, and isocyanates. Thermally activated organic peroxides, such as di-t-butyl peroxides, can also be used for cross-linking by heat.

5 The cross-linking agents are included in amounts from about 0.002 pph (parts per 100 parts of acrylate monomers, that is, the alkyl acrylate and the optional co-monomer) to about 2 pph, and preferably from about 0.01 pph to about 0.5 pph. The amount used will depend upon the amount of functionality and molecular weight of the cross-linking agent, and the desired properties of the
10 adhesive. For electrically conductive adhesives it is preferred that the amounts of crosslinking agents and the chain transfer agents is limited so that the adhesive flows sufficiently during bonding so that the conductive particles can come into contact with each other to provide conductive pathways. Preferred heat activated electrically conductive adhesives have a tan delta of greater than 1 at 140°C and
15 above, measured at 1 radian/sec. At these temperatures the adhesives have flow properties similar to a viscous liquid.

Tackifying agents can also be added to the syrup to enhance adhesion to certain low energy surfaces such as those on olefinic substrates. Useful tackifying agents include hydrocarbon resins, hydrogenated hydrocarbon resins, phenol
20 modified terpenes, poly(t-butyl styrene), rosin esters, vinyl cyclohexane, and the like. Suitable tackifying resins are commercially available and include, for example, those sold under the Regalrez™ and Foral™ trade designations from Hercules, such as Regalrez™1085, Regalrez™1094, Regalrez™6108, Regalrez™3102, and Foral™85.

25 When used, tackifying agents can be used in amounts from about 1 to about 100 pph, preferably 2 to 60 pph, and more preferably, 3 to 50 pph.

Other adjuvants can be included in the composition either before or after making the syrup in amounts needed to effect the desired properties as long as they do not affect the polymerization and the desired end properties. Useful adjuvants
30 include dyes, pigments, fillers, and thermally conductive particles.

The adhesives are useful in the preparation of pressure-sensitive adhesive tapes. The tapes can be prepared as transfer tapes in which the screen printed adhesive is typically provided on a liner coated on both sides with a release coating. The tapes can also be prepared a tape having the adhesive permanently adhered to the backing. Tapes with the adhesive permanently adhered to the backing can be prepared either by laminating the adhesive of a transfer tape to the backing, or by coating the composition onto the backing and curing the adhesive on the backing. Tapes can also be double coated tapes wherein both sides of the backing have a layer of adhesive on them. Useful backing materials include polymeric films, such as those made from cast and oriented polyesters, cast and oriented polypropylene, polyethylene, paper, metal foils, woven and nonwoven fabrics, and foams, such as those made from polyolefins and acrylics. Examples of suitable acrylic foams are those disclosed in U. S. Patent No. 4,415,615 (Esmay, et al.). Suitable polyolefin foams include cross-linked polyethylene and polyethylene/EVA foams.

The adhesives of the invention are particularly useful for screen printing directly onto a substrate when it is desired to have adhesive only on select areas of the surface. One such substrate is a flexible electrical circuit. Flexible electrical circuits generally comprise a polymeric film coated with electrically conductive metals such as copper, which has been etched to provide electrically conductive circuit traces. The polymeric films are typically polyimide, although other types of films such as polyester are also used. Suitable flexible circuits are commercially available from such sources as Nippon Graphite, Ltd. Flexible circuits are also described in U.S. Patent Nos. 4,640,981, 4,659,872, 4,243,455, and 5,122,215. For these types of applications, preferred compositions for the adhesives comprise from about 25 to 95 parts alkyl acrylate monomers and 75 to 1 parts of at least one reinforcing monomer that does not contain acid, and 1% to 10% by volume of electrically conductive particles. Preferably, the co-monomer is isobornyl acrylate and the electrically conductive particles are present in amounts of about 1% to 5% by volume.

Flexible electrical circuits are used in electronic devices where an electrical and mechanical interconnection must be made, such as between two circuit boards,

or between a circuit board and a liquid crystal display (LCD). Such connectors are useful in a variety of electronics such as in calculators, computers, pagers, cellular phones, and the like.

The adhesive is also useful as a damping polymer. In use the polymer may
5 be used as a free layer damper in which the adhesive is used by itself, or as a constrained layer damper. In the constrained layer damper, the adhesive is bonded to a material having a higher modulus than the adhesive. Examples of useful constraining layers include, but are not limited to, metals such as aluminum, stainless steel, cold rolled steel, and the like. In practice, the adhesives of the
10 invention can be screen printed directly onto the constraining layer. When the adhesive material is not pressure-sensitive, the adhesive can be bonded to the constraining layer by heating to slightly temperatures, for example, 70°C, and applying pressure on the adhesive.

In the method of practicing the invention, a syrup is formed by partially
15 polymerizing a mixture of the alkyl acrylate, the optional co-monomer, a free radical initiator, and a chain transfer agent. Useful free radical initiators for making the syrup include the above-described photoinitiators as well as thermal initiators. Suitable thermally activated free radical initiators are commercially available such as those available from DuPont Company under the VAZO trade designation. Specific
20 examples include Vazo™64 (2,2'-azobis(isobutyronitrile) and Vazo™52. Useful amounts can vary from about 0.01 pph to about 2 pph. Preferably, the partial polymerization is effected by ultraviolet lamps with a photoinitiator. More preferably, the partial polymerization is effected by ultraviolet lamps having a majority of their emission spectra between about 280 and 400 nanometers, with a
25 peak emission at about 350 nanometers, and at an intensity of less than amount 20 milliWatts per square centimeter (mW/sq cm). A composition comprising the syrup, additional photoinitiator, optional cross-linking agent(s), and any other desired adjuvants is then mixed, optionally degassed, and coated onto a substrate. Suitable substrates include polymeric films, such as polyester films, paper, metal,
30 ceramic, glass, flexible electrical circuits, and the like. The substrate is optionally treated with a release coating material such as silicone release agents, TEFLON™

coatings, perfluoropolyether coatings, and the like. The coated composition is then exposed to ultraviolet lamps in a low oxygen atmosphere, that is, containing less than about 500 parts per million oxygen (ppm), and preferably less than about 200 ppm to cure the composition to a pressure bondable adhesive. Alternatively, the
5 composition can be cured by other means such as exposure to electron beam radiation. Optionally, the cured adhesive can be exposed to other sources of energy such as heat, electron beam, high intensity ultraviolet, and the like to further cross-link the adhesive.

The following non-limiting examples illustrate specific embodiments of the
10 invention.

TEST METHODS

Electrical Conductivity

This test is a measurement of the electrical resistance through the adhesive
15 bond and a conducting circuit. Resistance readings should be less than about 100 Ohms, and preferably less than about 20 Ohms.

A test sample is prepared by bonding a straight line 8 mil (0.2 mm) pitch adhesive coated flexible circuit (3M™ Brand Heat Seal Connector without adhesive, available from Minnesota Mining & Manufacturing Co., St. Paul, MN) between a
20 printed circuit board (FR-4 test board) and an ITO coated glass plate (20 Ohms/square sheet resistivity available from Nippon Sheet Glass, Japan). The circuit traces the flexible electrical circuit are aligned to the corresponding traces on the circuit board and bonded by hand pressure for a pressure-sensitive adhesive or by hot bar bonded for a heat activated adhesive. Hot bar bonding is accomplished
25 with a 3 mm by 25.4 mm thermode (TCW 125, from Hughes Aircraft) set at 145°C and 800 psi (5516 kiloPascals) for 10 seconds. The other end of the flexible circuit is bonded to the ITO coated side of the glass plate. For samples that are flood coated, that is, have adhesive covering the entire flexible circuit, only the area contacted by the thermode is bonded to the circuit board. For screen printed
30 samples, only certain areas are printed with the adhesive.

Electrical resistance of the adhesive interconnection is measured by the four-wire method using the principles described in ASTM B 539-90 such that the net resistance not due to the interconnection is minimized to approximately 150 milliOhms. Results include the average resistance (AVG), the minimum resistance (MIN), and the maximum resistance (MAX). Samples are tested after bonding (INIT) and after aging at 60°C and 95% relative humidity for 10 days (AGED).

90° Peel Adhesion

This test is conducted by adhering a flexible electrical circuit with the adhesive to either an FR-4 circuit board or to an indium tin oxide (ITO) glass plate having 20 Ohms/square sheet resistivity (available from Nippon Sheet Glass, Japan) by hand for a pressure-sensitive adhesive, or using a 3 mm by 25.4 mm pulsed heat thermode (TCW 125, from Hughes Aircraft) set at 145C and 800 psi (5516 kiloPascals) for 10 seconds. The circuit board is mounted in a fixture in the lower jaw of an Instron™ Tensile Tester so that the flexible circuit, mounted in the upper jaw, would be pulled off at a 90° angle. The width of the flexible circuit is 1.9 to 2.5 cm. The jaw separation speed was 2.54 millimeters per minute and results are recorded in grams/centimeter. Samples are tested after bonding (INIT) and after aging at 60°C and 95% relative humidity for 10 days (AGED) and results are reported in grams/centimeter (g/cm).

Molecular Weights

The molecular weight of the syrup is determined by conventional gel permeation chromatography. The instrumentation includes a Hewlett-Packard Model 1090 Chromatograph, a Hewlett-Packard Model 1047A Refractive Index Detector, and a variable wavelength UV detector set at 254 nanometers. The chromatograph was equipped with an ASI Permagel 10 micron column. The system was calibrated with Polystyrene standards from Pressure Chemical Co. The signal was converted to digital response using Nelson Analytical hardware and software and the molecular weight (weight average) is determined software from Polymer Labs. GPC test methods are further explained in Modern Size Exclusion Liquid Chromatography: Practice of Gel Permeation Chromatography, John Wiley and Sons, 1979.

The samples are prepared by pre-treating with diazomethane in diethyl ether. After drying, the samples are dissolved in tetrahydrofuran (THF) at a concentration of 2.0 milligrams per milliliter of THF and filtered through a 0.2 micrometer Teflon™ filter. Samples are injected into the columns at volumes of 100 micro-liters and eluted at a rate of 1 milliliter per minute through columns maintained at 21°C.

Viscosity, Measured Yield Point, Calculated Yield Point

The rheological characteristics are determined on a Carri-Med CS Rheometer. The rheometer is of the cone and plate type with a cone angle of 2:00:00 deg:min:sec, and a cone diameter of 4.0 cm. The gap is 55 microns, and the system inertia is 203.3 dyne/square centimeter. The starting and end temperatures are 25°C. The starting stress is 10.00 dyne/square centimeter, and the end stress is 1750 dyne/square centimeter. Viscosity and yield points are measured and data is reported as (a) Viscosity in centipoise (cps), (b) Measured Yield in dynes/sq. cm., and (c) Calculated Yield in dynes/sq cm. The Calculated Yield is determined using the Casson model.

Example 1 and Comparative Example C1

A pressure-sensitive adhesive composition was prepared by mixing 67 parts isooctyl acrylate (IOA), 33 parts isobornyl acrylate (IBA), 0.1 pph (part per 100 parts of acrylate and co-monomer) benzil dimethyl ketal photoinitiator (Escacure™KB-1 photoinitiator from Sartomer), and 0.1 pph carbon tetrabromide in a glass jar, purging the jar with nitrogen, and exposing to ultraviolet radiation from fluorescent black lights which have at least 90% of their spectral output between 300 and 400 nanometers with a peak emission at about 350 nanometers until a viscous syrup having a viscosity estimated to be about 2000 to 3000 centipoise was formed. To the syrup was added 0.1 pph of 1,6-hexanedioldiacrylate (HDDA) and 0.2 pph of a second photoinitiator (Lucirin TPO available from BASF). The adhesive was then screen printed onto a polyester film using a 60 mesh screen on a rotary screen printer (X-Cel Rotary Screen Printer from Stork). The adhesive formed a fairly uniform coating on the substrate with a few bubbles, and slight stringing of the adhesive.

Comparative Example C1 was prepared as for Example 1 except that 0.04 pph KB1 photoinitiator was used in preparing the syrup and no chain transfer agent was used. The resulting adhesive did not screen print well and exhibited stringing between the screen and the substrate which caused large bubbles and holes in the adhesive coating and a very non-uniform coating.

The examples were cured by exposing the coated adhesives to medium pressure mercury lamps to form an adhesive. The resulting adhesives were tacky and pressure-sensitive.

The adhesives of both examples were also tested for shear viscosity and shear elongation as a function of shear and extrusion rate. The shear viscosity was measured on a Bohlin CS Rheometer. Extensional viscosity was measured on an RFX viscometer from Rheometrics. Comparative Example C1 exhibited non-Newtonian rheological behavior that is typical of ultraviolet light cured adhesives as evidenced by shear thinning behavior and an apparent viscosity increase with increasing extension rate. The Trouton ratio, defined as the extensional viscosity/shear viscosity increased with increasing strain rate for C1. Example 1 exhibited a more Newtonian shear viscosity, which remained fairly constant with increasing shear, and the extensional viscosity and Trouton ratio were essentially constant as the strain rate was increased.

Examples 2 - 3

Heat activatable adhesives were prepared according to the procedure in Example 1 except that the syrup composition was 43 parts IOA, 57 parts IBA, 0.1 pph benzil dimethyl ketal photoinitiator, and 0.1 pph carbon tetrabromide. The light exposure time was varied to form syrups with a viscosity of about 16000 centipoise (cps) for Example 2 and about 2000 cps for Example 3. Viscosities were measured on a Brookfield RV Viscometer at a spindle speed of 5 rpm (Spindle #5) at room temperature. An additional 0.3 pph benzil dimethyl ketal photoinitiator and 0.1 pph HDDA were added to each of the syrups before screen printing.

Both adhesives were screen printed on an AMI 850 screen printer. The screen mesh, squeegee speed, squeegee angle, squeegee hardness were varied to

obtain the best coating possible with each of the adhesive compositions. The target coating thickness was 0.0254 mm (1 mil).

The composition of Example 2 was printable but required slow squeegee speeds to reduce the number of bubbles in the coating. The composition of
5 Example 3 had fewer bubbles during printing, but had flowed after printing to reduce edge definition. The coated adhesives were cured using two 15 Watt fluorescent black lamps (350 nanometer black lamps from Sylvania) in a nitrogen-rich atmosphere for about 6 minutes with the sample about 3 inches (7.62 cm) away from the lamps. The cured adhesives were essentially tack-free at room
10 temperature.

Example 4

A heat activatable adhesive composition was prepared by mixing 2 parts of the composition of Example 3 and 1 part of the composition of Example 2. The resulting composition had a viscosity estimated to be between about 5000 and 8000
15 centipoise. This composition produced the most well defined edges while being easily screen printed over a wide range of process conditions.

Examples 5 - 6 and Comparative Example C2

For Example 5, a heat activatable adhesive syrup having a viscosity of about 7680 cps (Spindle #5 at 5 rpm on Brookfield Viscometer) was prepared according
20 to the procedure of Example 1 having a composition for Example 5 of 40 parts IOA, 60 parts IBA, 0.1 pph benzil dimethyl ketal photoinitiator, and 0.1 pph carbon tetrabromide.

For Example 6 a pressure-sensitive adhesive syrup having a viscosity of about 6240 cps was prepared according to the procedure of Example 1 having a
25 composition of 65 parts IOA, 35 parts IBA, 0.1 pph benzil dimethyl ketal photoinitiator, and 0.1 pph carbon tetrabromide.

For Comparative Example C2, a heat activatable adhesive syrup having a viscosity of about 8080 cps was prepared as in Example 5 except that no carbon tetrabromide was added.

30 Before coating, all of the syrup compositions further included 0.05 pph HDDA and 0.3 pph Lucerin™TPO photoinitiator. Additionally, Example 6 also

contained 25 pph of a hydrocarbon tackifying resin (Regalrez™ 6108 available from Hercules).

The adhesives were screen printed. Examples 5 and 6 screen printed well with good edge definition. Comparative Example C2 exhibited severe stringing of the adhesive resulting in an unacceptable printed image.

Examples 5 and 6 exhibited rheological behavior similar to Example 1. The shear viscosity of these Examples, as a function of shear rate, remained relatively Newtonian up to about 100 seconds⁻¹. The shear viscosity, as a function of shear rate for Example C2 dropped rapidly, that is, about an order of magnitude over the same shear rate range. This rheological behavior is similar to Example C1.

Example 7

A heat activatable adhesive composition was prepared as in Example 6 with the addition of 2 pph fumed silica (Cab-O-Sil™ M5) to the syrup. The syrup was screen printed and had improved edge definition and substantially no flow of the coated adhesive before curing.

Examples 8 - 13 and Comparative Example C3

Heat activatable adhesive compositions were prepared according to the method of Example 1 using 40 parts IOA, 60 parts IBA, 0.1 pph KB-1, and the amount (AMT) in pph and type (TYPE) of chain transfer agent (CTA) shown in Table 1. The chain transfer agents used were CBr₄ (carbon tetrabromide), IOTG (iso-octyl thiol glycolate) and NDDM (n-dodecyl mercaptan). Various amounts of cross-linker (HDDA) in pph were added to the syrup as well as 0.3 pph TPO photoinitiator. Molecular weights were determined for Examples 9, 11, and C3. Examples 9 and 11 were screen printable. The rheology profiles, that is, shear viscosities, of Examples 10, 12, and 13 were similar to Examples 5 and 6 and should be screen printable. Example C3 is not expected to be screen printable because its rheological profile was similar to Examples C1 and C2.

Table 1

Ex	CTA - Amt/Type	HDDA	TPO	Molecular Weight
8	0.02/CBr ₄	0.025	0.3	NT*
9	0.04/CBr ₄	0.05	0.3	453,000
10	0.06/CBr ₄	0.025	0.3	NT
11	0.1/CBr ₄	0.025	0.3	263,000
12	0.1/NDDM	0.025	0.3	NT
13	0.1/IOTG	0.025	0.3	NT
C3	None	--	--	1,570,000

* NT - Not Tested

Example 13

5 A heat activatable conductive adhesive syrup was prepared according to the procedure of Example 1 by partially polymerizing 40 parts IOA, 60 parts IBA, 0.1 pph benzil dimethyl ketal photoinitiator, and 0.04 pph carbon tetrabromide. An adhesive composition was prepared by mixing the syrup with 0.05 pph HDDA and

10 dissolved. Then 4 pph fumed silica (Cab-O-Sil M5) and 20 pph conductive nickel spheres (CNS, air classified -20/+10 μ m available from Novamet, Inc.) were dispersed into the composition with a high shear mixer. The 20 pph of nickel spheres is 5% by volume of the adhesive composition. The adhesive composition was then screen printed onto a flexible electrical circuit (3M™ Brand Heat Seal

15 Connector without adhesive, available from Minnesota Mining & Manufacturing Co., St. Paul, MN) using a flat bed screen printer (Model 2BS Roll to Roll Screen Press System from Rolt Engineering Ltd.) with a 200 mesh polyester screen with 31° bias and 25 mil (0.635 mm) emulsion thickness and a 60 durometer rounded edge squeegee. The adhesive composition was printed in the print/flood mode with

20 a squeegee pressure of 20 psi (138 kiloPascals), 20 inches per second squeegee speed (50.8 cm/sec) and 20 inches per second (50.8 cm/sec) flood blade speed, and a minimum squeegee angle. The adhesive coating thickness was 43 to 53 μ m.

Th screen printed adhesive was cured by exposing the adhesive to fluorescent black lights as described in Example 1 at an intensity of about 4.5 to 5.5 milliWatts/square centimeter, and a total energy of about 335 to 350 milliJoules/square centimeter. The resulting adhesive was essentially non-tacky at room temperature but became tacky when heated to about 35°C. The printed flexible circuit was tested for electrical resistance and peel adhesion to both and ITO glass substrate and to a FR-4 circuit board. Test results are shown in Table 2.

Example 14

A heat activatable conductive adhesive was prepared as in Example 13 except that the amount of HDDA was reduced to 0.035 pph and the conductive nickel spheres were 2% gold coated conductive nickel spheres. The adhesive was then screen printed to a thickness of about 30 to 40 μm on the ends of the circuit traces of a flexible circuit. The adhesive was then cured as described above. This cure was followed by an exposure to mercury arc lamps for an exposure of 1100 milliJoules/square centimeter. The portion of the flexible circuit that was not adhesive coated had been coated with a non-adhesive protective cover coat (Enplate, from Enthone-OMI, Inc.). The resulting flexible circuit was tested for electrical resistance and peel adhesive as described above except that the bonding pressure was reduced from 800 psi (5516 kiloPascals) to 540 psi (3723 kiloPascals), and the AGED results reported are after 13 days of aging. Test results are shown in Table 2.

Table 2

	Example 13		Example 14	
	<u>INIT</u>	<u>AGED</u>	<u>INIT</u>	<u>AGED</u>
<u>RESISTANCE</u>				
AVG - Ohms	2.3	9.8	2.2	12.1
MIN - Ohms	2.1	4.4	2.0	5.9
MAX - Ohms	2.6	18.0	4.9	20.6
<u>Peel Adhesion</u>				
Glass - g/cm	826	1176	617	1883
Board - g/cm	1184	2836	834	1250

The results in Table 2 show that the adhesives of the invention are suitable for coating on to flexible circuits to provide electrical connections.

Example 15

5 A solution was prepared by blending (by weight percent) 30.1% IOA, 34.0% parts IBA, 16.02 parts isobutyl methacrylate polymer (ELVACITE™2045 from ICI Americas), and heating at 80C and stirring until the polymer was dissolved. The amount by parts was 37.6 parts IOA, 42.4 parts IBA, and 20 parts isobutylmethacrylate. An adhesive syrup composition was prepared by adding to
 10 the solution 3.2% fumed silica (M5 Cab-O-Sil™ silica from Cabot Corp.), 16 % gold coated nickel spheres (described in Example 13), 0.0192% photoinitiator (Lucerin™ TPO), 0.32% antioxidant (Irganox™ 1010 from Ciba Geigy), and 0.16 crosslinking agent (Ebecryl 230). The silica was mixed into the composition using a high shear mixer. The resulting syrup was tested for viscosity and yield point and
 15 data is shown in Table 3. A flexible circuit was prepared as in Example 14. The resulting circuit had was heat bondable, and had acceptable electrical resistance.

Examples 16-19

Adhesive compositions were prepared by according to the procedure of Example 15.

20 Example 16 had a composition of 52 parts IOA, 28 parts IBA, 20 parts styrene butadiene copolymer (K-resin 01 from Phillips Petroleum), 0.25%

photoinitiator (Lucerin™ TPO), 4% fumed silica (M5 Cab-O-Sil™ silica), 0.3% antioxidant (Irganox™ 1010), and 0.18% carbon tetrabromide.

Example 17 was prepared as in Example 16, except that the composition contained 32 parts IOA, 48 parts IBA, and 20 parts styrene butadiene copolymer.

5 Example 18 had a composition as in Example 15 except that it contained 52 parts IOA, 28 parts IBA, and 20 parts isobutyl methacrylate polymer.

Example 19 was prepared as in Example 18 except that it contained 32 parts IOA, 48 parts IBA, and 20 parts isobutyl methacrylate polymer.

Rheological test data is shown in Table 3.

10

Table 3

Example	Viscosity (cps)	Measured Yield (dynes/sq. cm)	Calculated Yield (dynes/sq. cm)
15	968.2	254.8	522.0
16	1038	44.97	613.0
17	1187	289.8	464.3
18	771.2	132.4	260.4
19	1371	202.4	427.9

15 It will be apparent to those skilled in the art that various modifications and variations can be made in the method and article of the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A screen printable adhesive composition comprising:
 - (a) 25 to 100 parts by weight of at least one alkyl acrylate monomer;
 - 5 and
 - (b) 0 to 75 parts by weight of at least one reinforcing comonomer;wherein said composition is substantially solvent free and has a yield point of less than 600 dynes/square centimeter and a viscosity of less than 4000 centipoise.
- 10 2. The adhesive composition of claim 1, further comprising a chain transfer agent.
3. The screen printable adhesive composition of claim 1, wherein said chain transfer agent is present in an amount of from 0.01 to 1 pph.
4. The screen printable adhesive composition of claim 3, wherein said
15 chain transfer agent is selected from carbon tetrabromide, n-dodecyl mercaptan, or isooctyl thioglycolate.
5. The screen printable adhesive composition of claim 1 or claim 2, wherein said composition further comprises a thixotropic agent.
6. The screen printable adhesive composition of claim 5, wherein said
20 thixotropic agent is silica.
7. The screen printable adhesive composition of claim 1 or claim 2, further comprising an effective amount of an electrically conductive agent.
8. The screen printable adhesive composition of claim 7, wherein said electrically conductive agent is selected from nickel, silver, copper, or gold
25 particles.
9. The screen printable adhesive of claim 1 or claim 8, further comprising a polymer, copolymer, or macromer having a weight average molecular weight of less than 100,000.
10. The screen printable adhesive composition of claim 1, wherein
30 said composition further comprises a crosslinking agent.

11. A process for preparing an adhesive comprising the steps of:
- (a) providing the screen printable adhesive composition of claim 1;
- and
- (b) exposing said composition to ultraviolet radiation to polymerize
- 5 said composition.
12. The adhesive produced by the process of claim 11.
13. A tape comprising:
- (a) a layer of the adhesive of claim 7; and
 - (b) a tape substrate.
- 10 14. The tape of claim 13, wherein said tape substrate is a plastic film and wherein a plurality of electrically conductive areas overlay the plastic film and underlay and contact said pressure sensitive adhesive.

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 96/11508

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09J4/00 C09J7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 148 199 (LOCTITE) 16 March 1973 see the whole document ---	1,5,6,9, 10
X	DATABASE WPI Week 9403 Derwent Publications Ltd., London, GB; AN 94023080 XP002016485 & JP,A,05 331 427 (SEKISUI CHEM IND) , 14 December 1993 see abstract ---	1,9-12
A	EP,A,0 210 309 (HITACHI CHEMICAL) 4 February 1987 see column 4, line 35 - column 5, line 56 --- -/--	1-4,9-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/11508

C.(Continuation) D. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	DATABASE WPI Week 9316 Derwent Publications Ltd., London, GB; AN 93-131383 XP002016688 & JP,A,05 070 605 (ASAHI CHEM) , 23 March 1993 see abstract -----	1,5-14

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US-A-4587313	06-05-86	NONE	
